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(54) **Title:** A METHOD FOR THE PURIFICATION OF WATER BY MEANS OF FILTRATION USING A MICRO OR ULTRA FILTRATION MEMBRANE

(57) **Abstract:** The present invention relates to a method for purification of water by means of dead-end filtration using a micro or ultra filtration membrane, wherein the filtration is periodically interrupted to cleanse the membrane, wherein prior to, during the start or during each filtration period a filtration aid is added to the water to be purified, so that a layer of said filtration aid is deposited on the membrane, wherein the filtration aid comprises particles of an ion-exchange resin having a particle size of 0.5 to 50 μm. The filtration aid preferably is added in a high concentration prior to or during the start of each filtration period. With the method according to the invention the water is completely freed in a single purification step from suspended and colloidal matter and specific dissolved elements such as for instance hardness, manganese, ammonium, assimilable organic carbon and colour.

A method for the purification of water by means of filtration using a micro or ultra filtration membrane

The present invention relates to a method for the purification of water by means of dead-end filtration using a micro or ultra filtration membrane, wherein prior to, during the start or during each filtration period a suspension of a filtration aid is added to the water to be purified, so that a layer of said filtration aid is deposited on the membrane.

Micro and ultra filtration are known techniques for the purification of water that are used for the production of for instance drinking water, domestic and industrial water.

In micro filtration and ultra filtration water (feed) is let to pass along a polymeric or ceramic membrane. During the filtration stage water, under the influence of pressure as driving force, is pressed through the membrane (permeate) whereas suspended matter, colloidal matter and large organic molecules remain on the membrane. The quantity of water that passes a square meter of membrane per hour is called flux. The particles that remain cause fouling that is shown in an increase of the pressure drop over the membrane. Periodically therefore the membrane is cleansed by flowing the membrane in opposite direction for a short while (often called "backflush"). Clean water is pressed from the permeate side to the feed side, as a result of which the layer of dirt is removed and discharged (retentate). The membrane can also be cleansed by letting water and/or water and air pass along the dirt layer on the membrane at high speed (often called "forward flush" or "air flush"). Because such cleansings often leave a small quantity of pollutants behind, a cleansing using chemicals is regularly carried out (often called "chemical cleansing" or

"enhanced backwash"). The filtration process is therefore divided into several cycles, wherein a filtration cycle is followed by a rinsing cycle. After a number of filtration and rinsing cycles a chemical cleansing is carried out.

During the filtration stage the membranes can be operated in "cross-flow" or "dead-end" mode. In cross-flow mode only a part of the feed water is discharged as permeate during the filtration stage, while the remaining part leaves the membrane element again, whereas in dead-end mode all the feed water is pressed through the membranes. The membranes can be designed like tubular, capillary or flat membranes.

The great advantage of micro and ultra filtration is that by using said techniques a very good product quality is achieved in a single process step. The removal of suspended and colloidal matter (including bacteria and viruses) can be called absolute in comparison with conventional purifications. In addition said product quality is independent of the changes in the feed. The broad applicability renders micro and ultra filtration attractive for the production of both drinking-water and domestic and industrial water, or as pre-purification in the production of demi-water. As a result of developments in the membrane technology and improved operation (including cleansing regimes) the treatment of a large range of water qualities is technically and economically feasible.

In a number of cases the above-mentioned techniques cannot be used because of a high fouling rate and/or an instable operation. In such cases the pressure over the membrane recovers insufficiently after a backflush and a chemical cleansing. The fouling will then be so extreme that the membranes periodically have to be thoroughly cleansed or in some cases have to be replaced. In such cases a dose of a filtration aid may be a solution to stabilise the process. Several techniques have been described to that end:

- "In-linecoagulation": in this technique a coagulation agent is continuously dosed to the feed flow. Due to the coagulation agent small particles present in the water are flocculated to form larger ones. As a result said particles may clog up the pores of the membrane to a lesser extend. [P. van der Maas et al, 1999.]
- "Coating/body feed": in this technique a particles suspension is continuously dosed to the feed flow. Said particles (in most cases activated carbon) disrupt the cake building on the membrane as a result of which said cake is more easily separated from the membrane during cleansing. [Y. Matsui, 2000.]
- "Pre-coating": in this technique a suspension having a high concentration of particles is dosed on the membrane prior to the start or during the start of the filtration cycle. The particles form a protective layer or pre-coat on the membrane. During the filtration cycle suspended matter in the feed water is trapped by the pre-coat instead of by the membrane. During backflush the pre-coat layer is separated from the membrane and the trapped layer is discharged with the pre-coat particles. [G. Galjaard et al, 2000.]

Although micro and ultra filtration are very suitable for the removal of suspended and colloidal matter, dissolved elements such as for instance ions (salt), humic acids, pesticides/herbicides and organic micro pollutants (a number of specific organic carbon compounds) are not retained by micro and ultra filtration membranes, or only to a small extent.

In the production of high-quality drinking water or industrial water (for instance demineralised water for refrigeration purposes) additional purification steps are used for the removal of said dissolved elements. In

such a purification micro and ultra filtrations can be considered pre-treatment- or "polishing" techniques that act as a "disinfection screen" for the following steps. The use of several purification steps renders the water production expensive.

As noted above, the use of micro or ultra filtration will often be considered in the purification of water, especially when disinfection is necessary. In many cases, however, also a part of the dissolved elements will have to be removed as well, as a number of said dissolved elements may cause problems. For instance ammonium and assimilable organic carbon (AOC) may cause the growth of bacteria in the distribution system, in the installations of the customers or in the subsequent purification. Another dissolved substance that may cause problems is for instance manganese which after oxidation may form a black deposit that is difficult to remove.

Recently the use was suggested of separate ion exchange columns for the removal of dissolved substances [C. Charnock, 2000 and S.G.J. Heijman et al 1999] and colour [S. Verbych et al 2000, W.H. Höll et al, 2000]. So, here an additional step in the purification of water is used.

It is therefore an object of the invention to provide a method with which both suspended and colloidal material and dissolved elements can be removed in a single purification step.

According to the invention this object is achieved by dosing ion-exchange particles to the membrane prior to or during the filtration, in water purification by means of dead-end filtration using a micro or ultra filtration membrane.

Thus the invention provides a method for the purification of water by means of dead-end filtration using a micro or ultra filtration membrane, wherein the filtration is periodically interrupted to cleanse the membrane

and wherein prior to, during the start or during each filtration period a filtration aid is added to the water to be purified, so that a layer of said filtration aid is deposited on the membrane, characterized in that the filtration aid comprises particles of an ion-exchange resin having a particle size of 0.5 to 50 μm.

With the method according to the invention the water is completely freed in a single purification step from suspended and colloidal matter and specific dissolved elements such as for instance hardness, manganese, ammonium, assimilable organic carbon and colour.

The method according to the invention can be carried out using the known micro and ultra filtration membrane materials and designs.

The membrane may for instance be a spiral wound membrane, a flat membrane or a capillary membrane. For large-scale production (>250 m^3/h) it is preferred to use compact membrane modules that are provided with a large number of capillary membranes (hollow fibres, having a fibre diameter of for instance 0.5 mm). Examples of materials of such capillary membranes are hydrophilic polyether sulphone (PES), polysulphone (PS), polypropylene (PP), cellulose acetate (CA), polyacrylonitrile (PAN) polyvinylidene fluoride (PVDF) or polyvinyl pyrrolidine (PVD).

In carrying out the method of the invention the membranes are operated in "dead-end" mode.

The ion-exchange particles may suitably be added to the water to be purified in the form of a suspension of the particles in water.

Both cation-exchange resins and anion-exchange resins can be used as ion-exchange resin in the method of the invention. It is also possible to use a mixture of said resins. The choice of the resin to be used is determined by

the analysis of the water to be purified and the intended use of the purified water.

The ion-exchange resin particles have a particle size of 0.5-150 μm, preferably 0.5-20 μm. The particle size of the ion exchange resin is considerably smaller than the particle size of 0.2-1.2 mm of the common ion-exchange resins in separate columns for the removal of substances. The suitable particle size of the resin to be used according to the invention depends on the type of synthetic resin and the desired retention of the specific dissolved substances.

The ion-exchange resins to be used preferably are micro-porous. Examples of suitable ion-exchange resins include Duolite AP 143/1093 (by Rohm & Haas) and Amberlite IRP69/IRP64 (by Rohm & Haas).

The layer of ion-exchange resin particles may be deposited by continuously dosing the particles during each filtration period. The suspension of resin particles can also be dosed prior to or during the start of each filtration period. When the suspension is added prior to the start of the filtration period, a layer of deposited particles is present on the membrane prior to the start of the filtration. The layer of resin particles preferably is applied to the membrane by dosing a suspension of ion-exchange resin particles having a relatively high concentration (pulse dose) during a short period (<5 minutes in a filtration period of 15 to 60 minutes), prior to or at the start of the filtration period. After said pulse dose, the dosing of the suspension of particles can also be continued in a low concentration during the filtration cycle. The concentration of resin particles in the suspension is determined by the set dose time and the wanted thickness of the layer. A suitable thickness of the layer is 3 to 5 times the diameter of the dosed synthetic resin particles.

After a certain filtration time or after a certain pressure difference over the

membrane has been achieved, the membrane is backflushed. The layer of particles carrying the trapped substances (both suspended and colloidal matter and dissolved substances) is separated from the membrane and is flushed out of the membrane device. The concentrate flow with separated particles is received in a separation tank wherein the synthetic resin is separated from the remainder of the fluid. The synthetic resin particles are transported back to the suspension tank from where the particles can be dosed again. After the particles have been used a number of times, they are regenerated with a salt solution after which they can be used again.

Literature

Chang Y-J, Choo K-H, Benjamin., M.M., Reiber S., *Combined adsorption - UF process increases TOC removal,* Journal AWWA vol 90, 1998.

Galjaard G., Paassen van J., Buijs P., Schoonenberg G., *Enhanced Pre-Coat Engineering. The Solution for Fouling?*, Proceedings of the Conference on Membranes in Drinking and Industrial Water Production, Volume 1, page 605-610, ISDN 0-86689-060-2, October 2000, Desalination Publications l'Aquila, Italy.

Galjaard G., Schoonenberg F., de Jonge J., *Meetprotocol Quick-Scan: vergelijken van MF/UF membraanprestaties*. Kiwa rapport SWE 98.008, December 1998.

Maas P. van der, Leiting E., Dost S., Eppinga E., van Hoof S., *Customizes water Supplies: producing high quality process water from surface water using membrane technology,* Proceedings AWWA membrane Technology Conference, Long Beach (Calif.) 1999.

Y. Matsui, *Effect of operational modes on the removal of a synthetic organic chemical by powderedactivated carbon during ultrafiltration*, Proceedings of the Conference on Membranes in Drinking and Industrial Water Production, Volume 1, page 215-224, ISDN 0-86689-060-2, October 2000, Desalinations Publications l'Aquila, Italy.

S. Verbych, M. Bryk, A. Alpatova, *Extraction of heavy metal ions from water solutions*, Proceedings of the Conference Innovations in Conventional and Advanced Water Treatment Processes, September 2000.

W.H. Höll, C. Bartosch, X. Zhao, S. He, *Elimination of trace heavy metals from drinking water by means of weakly basic anion exchangers,*

Proceedings of the Conference Innovations in Conventional and Advanced Water Treatment Processes, September 2000.

S.G.J. Heijman, A.M. van Paassen, W.G.J. van der Meer, R. Hopman, *Adsorptive removal of natural organic matter during drinking water treatment*, Water Science and Technology, Volume 40, No. 9, page 183-190, 1999, Elsevier GB.

C. Charnock, O. Kjonno, *Assimilable organic carbon and biodegradable dissolved organic carbon in Norwegian raw and drinking waters*, Water Res. Volum 34, No. 10, page 2649-2642, 2000 Elsevier GB.

Claims

1. A method for the purification of water by means of dead-end filtration using a micro or ultra filtration membrane, wherein the filtration is periodically interrupted to cleanse the membrane, wherein prior to, during the start or during each filtration period a filtration aid is added to the water to be purified, so that a layer of said filtration aid is deposited on the membrane, **characterized in that** the filtration aid comprises particles of an ion-exchange resin having a particle size of 0.5 to 50 μm.

2. A method according to claim 1, wherein prior to or during the start of each filtration period the filtration aid is added in a high concentration.

3. A method according to claim 1 or 2, wherein after filtration has taken place during a certain period of time or after a certain pressure drop has occurred over the membrane, the layer of ion-exchange resin including the pollutants trapped in it or on it is removed from the membrane, the ion-exchange resin is separated and optionally after regeneration, is used again as filtration aid.